Alkylideneamido-derivatives of Metals and Metalloids. Part III.[1] The Chemistry of Alkylideneamino(trimethyl)stannanes

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The chemistry of the alkylideneamino(trimethyl)stannanes $Me_3Sn{-}N{:}CR_2$ (R = CF_3, Bu^t, Ph, and p-$Me{\cdot}C_6H_4$) (R = CF_3 and p-$Me{\cdot}C_6H_4$ are new compounds) is described and it is clear that they have synthetic utility. They react with (i) protic compounds HA (to yield Me_3SnA), including HA = H_2O, ROH, $PhC{:}CH$, and C_6F_5H; (ii) metal hydrides LMH to give, usually, $Me_3Sn{-}ML$ complexes; (iii) metal chlorides LMCl to give, usually, $LM{-}N{:}CR_2$ complexes; and (iv) unsaturated compounds X:Y (to yield 1 : 1-insertion adducts, in an alkylideneamine catalysed reaction), including X:Y = PhNCO and $CH_2{:}CHCN$. With regard to (i) and (iv), reactivity decreases in the sequence $Me_3SnN{:}CBu^t{}_2 > Me_3SnN{:}CAr_2 > Me_3SnN{:}C(CF_3)_2$, but the reverse order holds for (iii); Me_3SnNMe_2 has similar reactivity to $Me_3SnN{:}CBu^t{}_2$.

IN Parts I [2] and II [1] aspects of the chemistry of alkylideneaminoboranes ($>B{-}N{:}CR_2$) were described. Elsewhere, alkylideneamido-derivatives of early [3] and late [4] transition metals were reported, *e.g.*, $(\pi{-}C_5H_5)_2Ti(Cl){-}N{:}CR_2$ (R = Bu^t or Ph) and *trans*- $[(Me_2PhP)_2Pt(H){-}N{:}C(CF_3)_2]$. Attention has previously been drawn to features of interest of the $(CF_3)_2C{:}N^-$ ligand in other contexts.[4]

Alkylideneamido-complexes of the Main Group metals or metalloids Be,[5] Zn,[6] B,[1,7,8] (and other refs. listed in ref. 1), Al,[9,10] Ga,[11] Si,[12-14] Ge,[12] Sn,[12] and As[14] have been characterised. The principal points of interest have

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been their synthesis and structures. With regard to the latter, attention has centred on (i) molecular aggregation: *e.g.*, dimers for many Group II and III compounds with $\mathrm{R_2CN^-}$ as a bridging ligand; and (ii) the angle at N: *e.g.*, for monomeric compounds linearity at N possibly due to $\mathrm{M}\overset{\longleftarrow}{=}\mathrm{N}$ π-bonding. Spectroscopic and diffraction studies relate to i.r.,[1,2,12–15] ^{1}H n.m.r. (magnetic equivalence of the two groups R),[7,12] electronic,[12] and mass[1,13,14] spectra, and *X*-ray data on $\mathrm{Ph_2C{:}NB(mesityl)_2}$,[15] and $\mathrm{LiAl(N{:}CBu^t{}_2)_4}$.[16] The chemistry of alkylideneamidometal compounds has been little explored: redistribution reactions of alkylideneaminosilanes with boron halides gave ligand exchange,[13] while insertion reactions of various unsaturated substrates into the Sn–N bond of alkylideneamidotin(IV) compounds have recently been described.[17] Additionally, the reaction of certain alkylideneamidotin(IV) compounds with NOCl has been reported.[18]

TABLE 1

Syntheses and reactions of alkylideneamino(trimethyl)stannanes

Reagents	Reaction conditions	Product (yield, %) ^{a}
$\mathrm{Me_3SnCl + LiN{:}C(CF_3)_2}$	1 : 1, $\mathrm{Et_2O}$, 0° 3 h	$\mathrm{Me_3SnN{:}C(CF_3)_2}$ (84)
$\mathrm{Me_3SnCl + LiN{:}CBu^t{}_2}$ ^{b}	1 : 1, $\mathrm{Et_2O}$, 0°, 3 h	$\mathrm{Me_3SnN{:}CBu^t{}_2}$ (73)
$\mathrm{Me_3SnCl + LiN{:}C(C_6H_4{\cdot}Me\text{-}}p\mathrm{)_2}$	1 : 1, $\mathrm{Et_2O}$, 20°, 12 h	$\mathrm{Me_3SnN{:}C(C_6H_4{\cdot}Me\text{-}}p\mathrm{)_2}$ (80)
$\mathrm{Me_3SnNMe_2 + HC{:}N(C_6H_4{\cdot}Me\text{-}}p\mathrm{)_2}$	1·1:1, n-$\mathrm{C_6H_{14}}$, reflux, 5 min	$\mathrm{Me_3SnN{:}C(C_6H_4{\cdot}Me\text{-}}p\mathrm{)_2}$ (95)
$\mathrm{Me_3SnN{:}C(CF_3)_2 + PhC{\vdots}CH}$	1 : 1, THF, reflux, 12 h	$\mathrm{Me_3SnC{\vdots}CPh}$ (35)
$\mathrm{Me_3SnN{:}C(CF_3)_2 + \pi\text{-}C_5H_5Mo(CO)_3H}$	1 : 1, THF, reflux, 6 h	$\mathrm{\pi\text{-}C_5H_5Mo(CO)_3SnMe_3}$ (52)
$\mathrm{Me_3SnN{:}C(CF_3)_2 +}$ *trans*-$\mathrm{(Ph_3P)_2Pt(Cl)H}$	1 : 1, xylene, reflux, 5 min ^{c}	*trans*-$\mathrm{(Ph_3P)_2Pt(SnMe_3)N{:}C(CF_3)_2 + (Ph_3P)_2Pt[(CF_3)_2C{=}NH]}$ (*ca.* 10) (67)
$\mathrm{Me_3SnN{:}CBu^t{}_2 +}$ *trans*-$\mathrm{(Ph_3P)_2Pt(Cl)H}$	1 : 1, $\mathrm{C_6H_6}$, reflux, 4 h	*trans*-$\mathrm{(Ph_3P)_2Pt(Cl)SnMe_3}$ (70)
$\mathrm{Me_3SnN{:}CPh_2}$ ^{d} $\mathrm{+ PhC{\vdots}CH}$	1 : 1, THF, reflux, 18 h	$\mathrm{Me_3SnC{\vdots}CPh}$ (51)
$\mathrm{Me_3SnN{:}C(C_6H_4{\cdot}Me\text{-}}p\mathrm{)_2 + C_6F_5H}$	1 : 1, reflux, 45 h	$\mathrm{Me_3SnC_6F_5}$ (57)
$\mathrm{Me_3SnN{:}C(CF_3)_2 + Bu^n{}_2NH}$	1 : 1·2, THF, reflux, 22 h	No reaction
$\mathrm{Me_3SnN{:}C(CF_3)_2 + (\pi\text{-}C_5H_5)_2TiCl_2}$	1 : 1, $\mathrm{C_6H_6}$, reflux, 1·75 h	$\mathrm{(\pi\text{-}C_5H_5)_2Ti(Cl)N{:}C(CF_3)_2}$ (90)
$\mathrm{Me_3SnN{:}C(CF_3)_2 +}$ *cis*-$\mathrm{(Ph_3P)_2PtCl_2}$	3 : 1, $\mathrm{C_6H_6}$, reflux, 17 h	*cis*-$\mathrm{(Ph_3P)_2Pt(Cl)N{:}C(CF_3)_2}$ (90)
$\mathrm{Me_3SnN{:}CBu^t{}_2 +}$ *cis*-$\mathrm{(Ph_3P)_2PtCl_2}$	2 : 1, $\mathrm{C_6H_6}$, reflux, 18 h	No reaction
$\mathrm{Me_3SnN{:}CPh_2 +}$ cis-$\mathrm{(Ph_3P)_2PtCl_2}$	2 : 1, $\mathrm{C_6H_6}$, reflux, 5 h	*cis*-$\mathrm{(Ph_3P)_2Pt(Cl)N{:}CPh_2}$ (95)
$\mathrm{Me_3SnN{:}C(CF_3)_2 + Br_2}$	2 : 1, n-$\mathrm{C_6H_{14}}$, 20°	$\mathrm{BrN{:}C(CF_3)_2}$ ^{e}
$\mathrm{Me_3SnN{:}C(CF_3)_2 + PhNCO}$	1 : 1, n-$\mathrm{C_6H_{14}}$, reflux, 5 h	$\mathrm{Me_3SnN(Ph)C({:}O)N{:}C(CF_3)_2}$ (85)
$\mathrm{Me_3SnN{:}CPh_2 + PhNCO}$	1 : 1, n-$\mathrm{C_6H_{14}}$, 20°, 0·5 h	$\mathrm{Me_3SnN(Ph)C({:}O)N{:}CPh_2}$ (95)
$\mathrm{Me_3SnN{:}CPh_2 + CH_2{:}CHCN}$	1 : 1, n-$\mathrm{C_6H_{14}}$, reflux, 2 h	$\mathrm{Me_3SnCH(CN)CH_2N{:}CPh_2}$ (95)
$\mathrm{HN{:}CPh_2 + PhNCO}$	1 : 1, n-$\mathrm{C_6H_{14}}$, 20°, 1 h	$\mathrm{PhNHC({:}O)N{:}CPh_2}$ (88)
$\mathrm{HN{:}CPh_2 + MeNCS}$	1 : 1, n-$\mathrm{C_6H_{14}}$, 20°, 12 h	$\mathrm{MeNHC({:}S)N{:}CPh_2}$ (100)

^{a} Quoted yields are of purified products. ^{b} Ref. 19. ^{c} The Pt–Sn compound was obtained from a separate experiment, using the alkylideneamidotin compound (1·25 mmol) and the platinum hydride (0·5 mmol) and heating under reflux (17 h) in $\mathrm{C_6H_6}$. ^{d} Ref. 12. ^{e} Incompletely characterised.

TABLE 2

Characterisation of new compounds

				^{1}H N.m.r.		
					Sn–Me	
Compound	M.p., °C	Appearance	ν(N=C) (cm^{-1})	Sn–Me(τ)	J^{117} (Hz)	J^{119} (Hz)
$\mathrm{Me_3Sn_2N{:}C(CF_3)_2}$	(51—53) *	Yellow liquid	1720 (s) ^{a}	9·48 ^{b}	56	58
$\mathrm{Me_3SnN{:}C(C_6H_4Me\text{-}}p\mathrm{)_2}$	(120—128) †	Yellow solid	1611 (sh), 1596 (s) ^{b}	9·69 ^{b} 7·71 ^{f}	54·5	57
$\mathrm{Me_3SnN(Ph)C({:}O)N{:}C(CF_3)_2}$	113—115(d)	White solid	1680 (s),^{c} 1643 (vs), 1595 (s) ^{c}	9·40 ^{g}	62	66
$\mathrm{Me_3SnN(Ph)C({:}O)N{:}CPh_2}$	93—95	White solid	1690 (w), 1614 (vs), 1579 (vs) ^{b}	9·55 ^{b}	56	58·5
$\mathrm{Me_3SnCH_2CH(CN)N{:}CPh_2}$		White solid	1624 (s),^{c} 2207 (m) ^{d,e}	9·48 ^{h}	55	63
trans-$\mathrm{(Ph_3P)_2Pt(SnMe_3)\{N{:}C(CF_3)_2\}}$	172—175(d)	Pale yellow solid	1662 (m) ^{c}	9·70 ^{h}	42 7 ^{i}	45
$\mathrm{(Ph_3P)_2Pt(Cl)(N{:}CPh_2)}$	175—190(d)	White solid	278 ^{e}			

^{a} Liquid film. ^{b} Benzene solution. ^{c} Nujol mull. ^{d} ν(C≡N) cm^{-1}. ^{e} ν(Pt–Cl) cm^{-1}. ^{f} Me-*p*. ^{g} THF solution. ^{h} $\mathrm{C_6D_6}$ solution. ^{i} J^{195}(Pt–Me).

* B.p. at 31 mmHg. † B.p. at 0·005 mmHg.

This paper deals with the chemistry of the alkylideneamido(trimethyl)tin(IV) compounds $\mathrm{Me_3Sn{-}N{:}CR_2}$ (R = $\mathrm{CF_3}$, $\mathrm{Bu^t}$,[19] Ph,[12] and *p*-$\mathrm{Me{\cdot}C_6H_4}$), as summarised in Table 1. By analogy with earlier studies on metal amides, these compounds probably provide a good model for the behaviour of other alkylideneamidometal compounds with, however, a higher than average reactivity. The reactions here reported refer to those with bromine and (i) protic compounds, especially acidic hydrocarbons, (ii) metal hydrides, (iii) heterocumulenes or $\mathrm{CH_2{:}CHCN}$, and (iv) transition metal halides. In connection with (iii), reactions of the free alkylideneamines were also examined. We have previously made an extensive study of the chemistry of metal amides $\mathrm{LM{-}NR_2}$ (see ref. 20 and earlier papers in that series) and especially of $\mathrm{Me_3Sn{-}NMe_2}$ (for a review, see ref. 21). The latter

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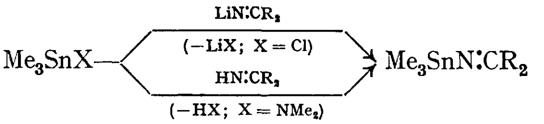
compound is characterised by having a weak (*E ca.* 40 kcal mol^{-1}) and polar $Sn^{\delta+}-N^{\delta-}$ bond,[22] and therefore reacts with polar substrates, including (i)—(iv); additionally it is a strong base and therefore presumably a powerful nucleophile. The objectives of the present work include a comparison with respect to their reactivity for each of (i)—(iv), of (a) amides and alkylideneamides, and (b) the four alkylideneamines with one another. Although it will be shown that imides are generally less reactive than amides, except for halogen/$N{:}CR_2$ or NR_2 exchange, they are both more selective and more widely available, particularly for late transition metal complexes,[4] and these two aspects make them synthetically useful.

The new compounds here reported are $Me_3SnN{:}C(CF_3)_2$, $Me_3SnN{:}C(C_6H_4{\cdot}Me\text{-}p)_2$, $Me_3SnN(Ph)C({:}O)N{:}CR_2$ (R = CF_3 or Ph), $Me_3SnCH_2(CN)CHN{:}CPh_2$, *trans*-$(Ph_3P)_2Pt(SnMe_3)N{:}C(CF_3)_2$, and $(Ph_3P)_2Pt(Cl)N{:}CPh_2$; details of their characterisation are in Table 2; the two platinum compounds have been prepared by other methods and will be discussed more fully elsewhere.[23]

The alkylideneamino(trimethyl)stannanes were prepared either by a lithium chloride or an amine elimination procedure [equation (1)]. Both of these methods have previously been used for the synthesis of other alkylideneamidometal compounds.[3,12]

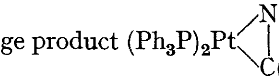


$$Me_3SnX \xrightarrow[\substack{HN{:}CR_2 \\ (-HX;\ X = NMe_2)}]{\substack{LiN{:}CR_2 \\ (-LiX;\ X = Cl)}} Me_3SnN{:}CR_2 \quad (1)$$

The use of 1,1-bis(trifluoromethyl)methyleneamidolithium [4] suffers from the disadvantage that forcing conditions cannot be employed since the compound is explosively unstable above 25°.[24] It is interesting that the corresponding tin complex $Me_3SnN{:}C(CF_3)_2$ showed no significant decomposition when heated at 100° for 5 h. It therefore has potential as an alkylideneamino-transfer agent under conditions where the use of the lithium reagent is ruled out; this has been successfully demonstrated (Table 1: reactions with Ti^{IV} and Pt^{II} chlorides) (see also comments below on Rh^{I} and Ir^{I}). The tin compound is not as reactive as the lithium analogue, but its higher selectivity is of value [*e.g.*, in the synthesis of $(Me_2PhP)_2Pt(Cl)N{:}C(CF_3)_2$ from the dichloride].[23]

Alkylideneamino(trimethyl)stannanes react with compounds having acid hydrogen, according to equation (2). With the less acidic compounds (*e.g.*, phenylacetylene), comparative experiments show that reactivity decreases in the sequence Me_3SnNMe_2 [25] $> Me_3SnN{:}CBu^t_2 > Me_3SnN{:}C(C_6H_4{\cdot}Me\text{-}p)_2 > Me_3SnN{:}CPh_2 > MeSnN{:}C(CF_3)_2$. This suggests that the nucleophilicity of the Sn–N compound is the controlling factor; certainly, basicities would be expected to follow the same sequence *e.g.*, first ionisation potentials (eV) are: Me_3SnNMe_2, (7·11) and $Me_3SnN{:}C(CF_3)_2$ (8·68).[26] Reactivity was greater in the polar solvent tetrahydrofuran (THF) than in n-hexane. The volatility of the eliminated amine or alkylideneamine does not appear to be important: *cf.*, b.p. $HN{:}C(CF_3)_2$, 16°, 760 mmHg and b.p. $HN{:}CPh_2$, 95°, 0·005 mmHg; also $Me_3SnN{:}C(CF_3)_2$ did not react when heated under reflux with $HNBu^n_2$ in THF for 22 h. For the more reactive reagents (*e.g.*, water), such distinctions are not clear. For example, $Me_3SnN{:}C(CF_3)_2$ reacts so readily with water that it fumes in air.

$$Me_3SnN{:}CR_2 + HA \longrightarrow Me_3SnA + HN{:}CR_2 \quad (2)$$

Behaviour with metal hydrides generally follows equation (2), but mechanistically may be unrelated to the above examples. Thus, $Me_3SnN{:}C(CF_3)_2$ is no less reactive than Me_3SnNMe_2 [27] towards $\pi\text{-}C_5H_5Mo(CO)_3H$. When the hydride has a second functional group, as in *trans*-$(Ph_3P)_2Pt(Cl)H$, the choice of alkylideneamine may qualititatively control the course of reaction. Thus, whereas $Me_3SnN{:}CBu^t_2$ affords *trans*-$(Ph_3P)_2Pt(Cl)SnMe_3$ [27] in high yield, the corresponding 1,1-bis(trifluoromethyl)methyleneamido-derivative yields mainly the Cl/$N{:}C(CF_3)_2$ exchange product  $(Ph_3P)_2Pt\langle^{NH}_{C(CF_3)_2}$,[28] probably *via* the tautomeric rearrangement [4] of $(Ph_3P)_2Pt(H)N{:}C(CF_3)_2$. Evidence for this intermediate is provided by the isolation of $(Ph_3P)_2Pt(SnMe_3)N{:}C(CF_3)_2$ when an excess of alkylideneamine was used. Of the available methods [27,29] for the synthesis of *trans*-$(Ph_3P)_2Pt(Cl)SnMe_3$ that from $Me_3SnN{:}CBu^t_2$ appears to be the best: the absence of side reactions is due to the low reactivity with respect to Cl/$N{:}CBu^t_2$ exchange (see below).

A number of metal chlorides (LM–Cl) were shown to undergo metathesis with alkylideneamidometal compounds [equation (3)], with the reactivity decreasing in the order $Me_3SnN{:}C(CF_3)_2 > Me_3SnN{:}CPh_2 \gg Me_3SnN{:}CBu^t_2$. The last named reagent was of comparable, but probably somewhat lower, reactivity to Me_3SnNMe_2.[30] This suggests that Sn–N heterolysis is involved in the rate-determining step. Electron-withdrawing (CF_3) and -delocalising (Ar) substituents would be expected to favour such bond-breaking and to stabilise the corresponding alkylideneamino-anion.

$$Me_3SnN{:}CR_2 + LM\text{–}Cl \longrightarrow LM\text{–}N{:}CR_2 + Me_3SnCl \quad (3)$$

Alkylideneaminosilanes have previously been used as alkylideneamino-transfer agents for preparing transition

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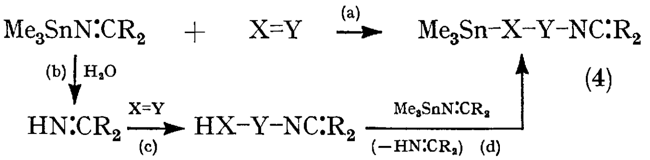
[29] M. Akhtar and H. C. Clark, *J. Organometallic Chem.*, 1970, **22**, 233.

[30] T. A. George and M. F. Lappert, *J. Chem. Soc.* (*A*), 1969, 992.

metal alkylideneamido-complexes.[5,31] However, the tin compounds are more reactive: *e.g.*, $(Ph_3P)_3RhN{:}C(CF_3)_2$ and *trans*-$(Ph_3P)_2Ir(CO)N{:}C(CF_3)_2$ have been obtained from corresponding co-ordinatively unsaturated chlorides under very mild conditions.[23]

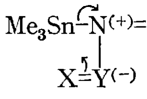
Alkylideneamino(trimethyl)stannanes are very much less reactive with respect to insertion reactions of unsaturated compounds [equation (4a)] than the amide Me_3SnNMe_2.[32] Furthermore it was found that traces of free alkylideneamine act as catalysts. This is explained in terms of the sequence shown in equations (4b)—(4d); a trace of moisture would cause the formation of alkylideneamine [equation 4(b)]. The rapid insertion of heterocumulenes such as PhNCO and MeNCS into the NH bond of diphenylmethyleneamine [equation 4(c)] has been demonstrated elsewhere [17] and is now confirmed. Similar catalysis (by dimethylamine) has been found for insertion reactions of Me_3SiNMe_2 with carbon dioxide or disulphide,[33] but is not a requirement for the more reactive tin(IV) analogue.[32] It is surprising that diphenylmethyleneamino(tri-n-butyl)stannane $Bu^n{}_3SnN{:}CPh_2$ is reported [7] to react instantly with 1,2-dipoles such as PhNCO, without mention of a catalyst.



$$\begin{tikzcd}
Me_3SnN{:}CR_2 + X{=}Y \arrow[rr, "(a)"] \arrow[d, "(b)"', "H_2O"] & & Me_3Sn{-}X{-}Y{-}NC{:}R_2 \\
HN{:}CR_2 \arrow[r, "X{=}Y", "(c)"'] & HX{-}Y{-}NC{:}R_2 \arrow[ur, "Me_3SnN{:}CR_2", "(-HN{:}CR_2)\ (d)"'] &
\end{tikzcd}$$

(4)

The reactivity order decreases in the series $Me_3SnNR_2 > Me_3SnN{:}CPh_2 > Me_3SnN{:}C(CF_3)_2$. This suggests that, as for reactions (2), the nucleophilicity of the Sn–N compound is important and an intermediate such as (I) may be involved. A polar transition state is supported by the observation that the reaction is progressively inhibited by the use of increasing amounts of a non-polar solvent; although an alternative explanation is that under these conditions even very slight hydrolysis to afford free alkylideneamine is less likely.



(I)

EXPERIMENTAL

Benzene and hexane were stored over sodium–potassium alloy and distilled from it before use. Diethyl ether and THF were distilled from sodium–benzophenone. Bromine was distilled from phosphorus(V) oxide. Solvents were rigorously degassed under vacuum before use and all reactions were performed under an atmosphere of dry, oxygen-free nitrogen. M.p.s., unless otherwise stated, were determined in sealed evacuated capillaries. Analyses were carried out by Mr. and Mrs. A. G. Olney of the Departmental Microanalytical Laboratory and by Alfred Bernhardt, West Germany. I.r. spectra were recorded using a Perkin-Elmer 457 instrument; ^1H n.m.r. spectra using a Varian A60 or HA100 instrument. Mass spectra were examined on an A.E.I. MS9 machine.

Bis(trifluoromethyl)methyleneamine,[24] trimethyltin chloride,[34] diphenylmethyleneamino(trimethyl)stannane,[12] *cis*-dichlorobis(triphenylphosphine)platinum(II),[34] *trans*-hydridochlorobis(triphenylphosphine)platinum(II),[35] and *N*-bromo-1,1-bis(trifluoromethyl)methyleneamine [24] were prepared according to published procedures. Other commonly available starting materials were dried and distilled before use, wherever possible.

Preparation of Bis(trifluoromethyl)methyleneamino(trimethyl)stannane.—Bis(trifluoromethyl)methyleneamine (8·7 ml, 87 mmol) was condensed into an ethereal solution of methyl-lithium (80 ml of 1M solution) at −196°. The mixture was allowed to warm to 0° to give a yellow solution which was stirred for 15 min. Trimethyltin chloride (16 g, 80 mmol) in diethyl ether (70 ml) was added dropwise to this lithium-reagent, keeping the temperature below 3°. The yellow solution with white solid was stirred for 1 h at 0° and then for a further 2 h at 20°. The volume of ether was reduced (to *ca.* 50 ml) and the lithium chloride was filtered off. The pale yellow solution afforded *bis(trifluoromethyl)methyleneamino(trimethyl)stannane* (22 g, 84%), b.p. 51°, 31 mmHg (Found: C, 22·1; H, 2·9; N, 4·1. $C_6H_9F_6NSn$ requires C, 22·0; H, 2·8; N, 4·3%).

*Preparation of Di-*t*-butylmethyleneamino(trimethyl)stannane.*[19]—t-Butyl cyanide (3·3 ml, 30 mmol) in n-hexane (60 ml) was added dropwise to a stirred solution of t-butyllithium (30 mmol) in hexane (70 ml) at 0°. The mixture was stirred at 0° for ½ h and then for a further 2 h at 20°. After recooling the mixture to 0°, trimethyltin chloride (5·80 g, *ca.* 30 mmol) in ether (50 ml) was added dropwise. The mixture was stirred for 1 h at 20°. Solvent was removed under reduced pressure and distillation of the residue gave the butylmethyleneamido-compound [19] (6 ml, 22 mmol, 73%), b.p. 46°, 0·01 mmHg, ν(CN) 1650 cm^{-1}.

*Preparation of Di-*p*-tolylmethyleneamino(trimethyl)stannane.*—This complex was routinely prepared from the appropriate lithium-reagent and trimethyltin chloride in a manner entirely analogous to that of the diphenyl derivative.[12] Yields of 80% were usually obtained (b.p. 117—119°, 10^{-3} mmHg). It was, however, difficult to remove traces of the free parent alkylideamine by this procedure.

A slurry of di-*p*-tolylmethyleneamine (3·56 g, 17 mmol) in hexane (25 ml) was added slowly to dimethylamino(trimethyl)stannane (3·78 g, 18·17 mmol) at room temperature. The reaction was exothermic. Immediately a yellow–green colour developed. The mixture was stirred for ½ h. The dimethylamine (authentic i.r. spectrum) was collected in a cold (−78°) trap. Solvent was removed under reduced pressure and a yellow–green liquid, solidifying on standing, was distilled and identified as *di-*p*-tolylmethyleneamino(trimethyl)stannane* (6·1 g, 97%) b.p. 120—128°, 0·005 mmHg (Found: C, 58·4; H, 6·3; N, 4·0. $C_{18}H_{23}NSn$ requires C, 58·1; H, 6·2; N, 3·8%).

Reactions of Alkylideneamidotin Compounds with Protic Compounds and Metal Hydrides.—(a) *Bis(trifluoromethyl)methyleneamino(trimethyl)stannane with phenylacetylene.* Phenylacetylene (0·8 g, 0·86 ml, 7·85 mmol) in hexane (5 ml) was added dropwise to the tin complex (2·5 g, 1·75 ml,

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7·85 mmol) in hexane (5 ml). The reaction mixture was heated under reflux (12 h). The i.r. spectrum showed that no reaction had occurred. Most of the hexane was removed *in vacuo*, THF (10 ml) was added, and the reaction mixture heated under reflux (4 h). Distillation yielded, after removal of solvent, (phenylethynyl)trimethylstannane [26] (0·69 g, 35%), b.p. 56—58°, 0·1 mmHg (Found: C, 49·5; H, 5·3. Calc. for $C_{11}H_{24}Sn$: C, 49·9; H, 5·3%) (parent ion in mass spectrum).

(b) *Bis(trifluoromethyl)methyleneamino(trimethyl)stannane with hydrido(π-cyclopentadienyl)tricarbonylmolybdenum*(II). The methyleneamidotin compound (1 ml, 4·89 mmol) in THF (10 ml) was added dropwise to the hydride (1·203 g, 4·89 mmol) in THF (10 ml). The solution was heated under reflux (6 h) and the solvent and unreacted metal-hydride were removed at 40°, 10^{-3} mmHg. Sublimation (100°, 10^{-3} mmHg) yielded π-cyclopentadienyl(trimethylstannyl)tricarbonylmolybdenum(II) [27] (1·03 g, 51·8%) (Found: C, 26·7; H, 2·9. Calc. for $C_{11}H_{14}MoOSn$: C, 26·6; H, 2·8%).

(c) *Bis(trifluoromethyl)methyleneamino(trimethyl)stannane with cyclopentadiene*. Freshly distilled cyclopentadiene (0·37 ml, 4·6 mmol) in THF (5 ml) was added dropwise to a solution of the methyleneamidotin compound (1·515 g, 0·80 ml, 4·6 mmol) in THF (10 ml). The reaction mixture was heated under reflux (4 h). Distillation afforded a few drops of the starting compound and a red involatile residue, which was not identified.

(d) *Bis(trifluoromethyl)methyleneamino(trimethyl)stannane with* trans-*hydridochlorobis(triphenylphosphine)platinum*(II). (i) 1 : 1 *Ratio of reactants in xylene*. The tin compound (0·1 ml, 0·5 mmol) in xylene (10 ml) was added to the hydride (0·38 g, 0·5 mmol) in xylene (20 ml). The almost colourless solution was heated to reflux temperature, whereupon the mixture became yellow and then red. After 5 min, heating was discontinued and the mixture was cooled to 45°. Solvent was removed *in vacuo* and benzene (5 ml) was added to give a red solution over a buff solid. These were separated by decantation using hexane. Recrystallisation (from CH_2Cl_2–n-C_6H_{14}) of the solid afforded the off-white 1,1-bis(trifluoromethyl)methyleneaminebis-(triphenylphosphine)platinum (0·3 g, 67%) (Found: C, 52·8; H, 3·6; N, 1·5. Calc. for $C_{39}H_{31}F_6NP_2Pt$: C, 52·9; H, 3·5; N, 1·6%) (authentic [4,23] i.r. spectrum).

(ii) *Excess of the tin compound in benzene*. The tin compound (0·25 ml, 1·25 mmol) was added to the hydride (0·38 g, 0·5 mmol) partially dissolved in benzene (20 ml). The mixture was heated under reflux (17 h), and the colour turned through pale-yellow to golden-yellow. Solvent and volatiles were removed *in vacuo* at room temperature to give a yellow gum. This was redissolved in a minimum quantity of benzene, and hexane was added to give a pale yellow solid and a yellow solution. The solid was filtered off and dried (1 h, at 10^{-3} mmHg). On the basis of analysis and comparison with a sample obtained by another route it was identified as trans-*bis(trifluoromethyl)methyleneamido(trimethylstannyl)bis(triphenylphosphine)platinum*(II) (*ca.* 10%) (Found: C, 48·7; H, 3·6; N, 1·5. $C_{42}H_{39}F_6NP_2PtSn$ requires C, 48·1; H, 3·8; N, 1·3%), m.p. 172—175(d). Solutions of the product were quite air and moisture sensitive.

(e) *Diphenyl-(or di-*p*-tolyl-)methyleneamino(trimethyl)stannane with phenylacetylene*. Phenylacetylene (0·35 ml, 0·32 g, 3·1 mmol) in THF (5 ml) was added to the tin compound (1·06 g, 3·01 mmol) in THF (10 ml). The mixture was heated under reflux (18 h). Distillation afforded phenylethynyl(trimethyl)stannane (0·4 g, 51·3%) (Found: C, 49·8 H, 5·3%) (authentic i.r. spectrum), b.p. 60—61°, 0·25 mmHg. In an exactly similar manner, the corresponding di-*p*-tolyl derivative also gave the tin acetylide (45%).

(f) *Diphenylmethyleneamino(trimethyl)stannane with* trans-*hydridochlorobis(triphenylphosphine)platinum*(II). The tin compound (0·172 g, *ca.* 0·66 mmol) was added to the hydride (0·378 g, 0·50 mmol) in benzene (35 ml). The mixture was heated under reflux (4 h) to give a ruby-red solution. The bulk of solvent was removed *in vacuo* and hexane added to give an orange-buff powder. This was filtered off, washed with hexane, and dried *in vacuo*. I.r. spectra revealed one main ν(Pt–Cl) (285 cm^{-1}) and the absence of ν(Pt–H).

(g) *Diphenylmethyleneamino(trimethyl)stannane with cyclopentadiene*. Cyclopentadiene (0·12 ml, an excess) in THF (5 ml) was added dropwise to the tin compound (0·327 g, 0·95 mmol) in THF (10 ml). The reaction mixture was stirred (12 h) at room temperature. Attempted distillation of the products under reduced pressure gave rise to decomposition products, including a red involatile residue.

(h) *Di-*t*-butylmethyleneamino(trimethyl)stannane with* trans-*hydridochlorobis(triphenylphosphine)platinum*(II). The tin compound [0·3 ml, 0·332 g, (1 mmol = 0·304 g)] was added to the hydride (0·756 g, 1·0 mmol) in benzene (40 ml) and the reactants were heated under reflux (4 h). The reddish brown reaction mixture was cooled to room temperature and most of the benzene removed *in vacuo*. Addition of hexane gave a yellow-buff solid, which was filtered off, washed with hexane, and then dried (1 h at 10^{-3} mmHg). Further solid was obtained by cooling the mother liquor to −20°. This (0·64 g, 70%) was identified as *trans*-chloro(trimethylstannyl)bis(triphenylphosphine)platinum(II) [27,29] (Found: C, 51·2; H, 4·5. Calc. for $C_{39}H_{39}ClP_2PtSn$: C, 51·0; H, 4·3%), m.p. 239—241°. I.r. (Nujol mull) showed ν(Pt–Cl) (280 cm^{-1}), but no ν (Pt–H). ^1H n.m.r. (C_6D_6) showed a 1 : 4 : 1 triplet (*J* 13 Hz: methyl groups on tin coupling with ^{195}Pt).

(i) *Di-*p*-tolylmethyleneamino(trimethyl)stannane with pentafluorobenzene*. Addition of pentafluorobenzene (0·7 ml, 1·12 g, 6·67 mmol) in THF (20 ml) to the tin compound (3·48 g, 6·67 mmol) gave a green-yellow solution. This was heated under reflux (45 h). Distillation afforded the colourless trimethyl(pentafluorophenyl)stannane [36] (0·91 g, 57%) (Found: C, 32·5; H, 2·8. Calc. for $C_9H_9F_5Sn$: C, 32·7; H, 2·7%), b.p. 32—34°, 0·08 mmHg. A white involatile residue in the distillation flash was identified (i.r.) as fluoro(trimethyl)stannane.

Reactions of Alkylideneamidotin Compounds with Metal Halides and with Bromine.—(a) *Bis(trifluoromethyl)methyleneamino(trimethyl)stannane with bis(π-cyclopentadienyl)titanium dichloride*. The tin compound (0·41 ml, *ca.* 2 mmol) was added by pipette to a stirred solution–slurry of the dichloride (0·498 g, 2 mmol) in benzene (35 ml). The mixture was heated under reflux ($1\frac{3}{4}$ h) to give a clear yellow solution. Most of the solvent was then removed *in vacuo* and hexane added to give yellow crystals of chloro-1,1-bis(trifluoromethyl)methyleneamidobis-(π-cyclopentadienyl)titanium(IV) [3] (0·67 g, 90%), which were filtered off, washed with hexane, and dried (1 h at 10^{-3} mmHg) (Found: C, 41·1; H, 2·7; N, 3·7. Calc. for $C_{13}H_{10}ClF_6NTi$: C, 41·3; H, 2·7; N, 3·7%), (authentic i.r. and ^{19}F n.m.r. spectra), m.p. 197—200°.

(b) *Bis(trifluoromethyl)methyleneamino(trimethyl)stannane with* cis-*dichlorobis(triphenylphosphine)platinum*(II). The

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tin compound (0·61 ml, 3 mmol) was added by pipette to a stirred solution–slurry of the platinum compound (0·790 g, 1 mmol) in benzene (50 ml). The mixture was heated under reflux (17 h). The volume of benzene was reduced to *ca.* 10 ml. Addition of hexane gave a pale yellow powder. This was filtered off, washed with hexane, and dried (1 h at 10^{-3} mmHg). It was identified as *cis*-chloro-1,1-bis(trifluoromethyl)methyleneamidobis(triphenylphosphine)-platinum(II)[4] (0·83 g, 90%) (Found: C, 52·0; H, 3·2; N, 1·6. Calc. for $C_{39}H_{30}ClF_6NP_2Pt$: C, 51·0; H, 3·3; N, 1·5%), m.p. 258—261°, ν(PtCl) 308 cm^{-1}, and ν(C=N) at *ca.* 1675 cm^{-1}.

(c) *Diphenylmethyleneamino(trimethyl)stannane with* cis-*dichlorobis(triphenylphosphine)platinum*(II). The tin compound (0·624 g, 1·92 mmol) was added to the dichloride (0·61 g, 0·81 mmol) in benzene (50 ml). The mixture was heated under reflux (5 h) and the bulk of the benzene was then removed *in vacuo*. Addition of hexane to the yellow solution yielded a yellow powder, which was filtered off, washed with hexane, and dried (1 h at 10^{-3} mmHg). A further small quantity of yellow solid was obtained upon cooling the filtrate to −20°. This was identified as *chloro-(1,1-diphenylmethyleneamido)bis(triphenylphosphine)-platinum*(II) (0·72 g, 95%) (Found: C, 60·8; H, 4·8; N, 1·7. $C_{49}H_{40}ClNP_2Pt$ requires C, 62·9; H, 4·3; N, 1·5%), m.p. 175—190° (d).

(d) *Lack of reaction between Di-t-butylmethyleneamino(trimethyl)stannane with* cis-*dichlorobis(triphenylphosphine)-platinum*(II). The tin compound (0·62 ml, >2 mmol) was added by pipette to a slurry of the platinum compound (0·790 g, 1 mmol) in benzene (50 ml). The reaction mixture was heated under reflux (18 h). The bulk of solvent was removed (to *ca.* 15 ml). Addition of hexane (30 ml) gave a white solid, which was filtered off, and washed with hexane. Examination of the solid (analysis, i.r.) showed it to be an almost quantitative yield of the platinum dichloride; the tin compound was not recovered.

(e) *Bis(trifluoromethyl)methyleneamino(trimethyl)stannane with bromine.* Bromine (0·28 ml, 5·0 mmol) was added by syringe to a stirred solution of the stannane (2·0 ml, 10 mmol) in hexane (10 ml) at room temperature. There was immediate decolourisation. The solution was stirred at room temperature (6 h). Distillation afforded (a) b.p. 37—42°, 760 mmHg, and (b) b.p. 69—70°, 760 mmHg. Fraction (a) turned brown upon exposure to fluorescent lighting, but fraction (b) remained colourless. I.r. examination of (a) (in hexane after photolysis) showed ν(C=N) at 1633 cm^{-1}, and absorptions due to CF_3, at 1320ms, 1303ms, 1228m,sh, 1248s, 1232s, and 1192s cm^{-1}. Fraction (b) was essentially pure hexane. Trimethyltin bromide was identified (i.r.) in the distillation residue. Before photolytic decomposition, fraction (a) probably contained *N*-bromo-1,1-bis(trifluoromethyl)methyleneamine.[24] In a separate experiment *N*-bromo-1,1-bis(trifluoromethyl)methyleneamine was distilled unchanged from bis(trifluoromethyl)methyleneamino(trimethyl)stannane. The tin compound was also recovered.

Reactions of Alkylideneamidotin Compounds and Related Compounds with Unsaturated Compounds.—(a) *Diphenylmethyleneamino(trimethyl)stannane with phenyl isocyanate.* Phenyl isocyanate (0·5 ml, 4·5 mmol) in hexane (15 ml) was added dropwise (20 min) to a stirred solution of the tin compound (1·552 g, 4·5 mmol) in hexane (15 ml). A slightly exothermic reaction ensued, with precipitation of white solid. The reactants were stirred at room temperature for a further ½ h. The white solid was filtered off and washed with hexane (40 ml) and then dried (1 h at 10^{-3} mmHg,) to give the 1 : 1 *adduct* (1·93 g, 95%) (Found: C, 59·4; H, 5·4; N, 6·2. $C_{23}H_{24}N_2OSn$ requires C, 59·6; H, 5·2; N, 6·1%), m.p. 93—95°. Similar products were obtained from parallel reactions with the di-*p*-tolyl- and di-t-butyl-derivatives; consistent analyses were not obtained in these particular small scale reactions, because of difficulty in removing hydrolysis and other impurities.

(b) *Bis(trifluoromethyl)methyleneamino(trimethyl)stannane with phenyl isocyanate.* Phenyl isocyanate (0·51 g, 0·46 ml, 4·2 mmol) in hexane (10 ml) was added to the tin compound (1·38 g, 4·2 mmol) in hexane (15 ml) at 20°. The solution was heated under reflux (5 h). Filtration afforded the 1 : 1 *adduct* (1·62 g, 85%) (Found: C, 35·8; H, 3·2; N, 6·3. Calc. for $C_{13}H_{14}F_6N_2OSn$: C, 34·9; H, 3·2; N, 6·3%). The mass spectrum showed the parent molecular ion.

(c) *Diphenylmethyleneamino(trimethyl)stannane with acrylonitrile.* Acrylonitrile (dried by distillation from CaH_2) (0·17 ml, 0·14 g, 2·56 mmol) was added dropwise by syringe to the tin compound (0·88 g, 2·56 mmol) in hexane (10 ml). The solution was heated under reflux (2 h). Solvent was removed at 20°, 10^{-7} mmHg to leave a yellow-white solid. Unreacted starting material was removed by washing with hexane to afford the white amorphous 1 : 1 *adduct* (0·99 g, >95%) (Found: C, 57·1; H, 5·9; N, 7·0. $C_{19}H_{22}N_2Sn$ requires: C, 57·5; H, 5·6; N, 7·1%). The mass spectrum showed the parent molecular ion.

(d) *Lack of reaction between diphenylmethyleneamino(trimethyl)stannane and benzonitrile.* Benzonitrile (0·11 ml, 0·106 g, 1·03 mmol) in hexane (10 ml) was added dropwise to a stirred solution of the tin compound (0·353 g, 1·03 mmol) in hexane (10 ml). There was no change (i.r.) after stirring at room temperature for 24 h, or after heating under reflux for a further 2 days.

(e) *Alkylideneamidotin compounds with other unsaturated compounds.* Preliminary experiments indicate adduct formation between these compounds and CS_2, CO_2, MeNCS, and PhNCS. The reactions with carbon disulphide are complex and various blue and yellow products were obtained.

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